# California Regional PM<sub>10</sub> and PM<sub>2.5</sub> Air Quality Study (CRPAQS)

# Statement of Work – CRPAQS Data Analysis Task 2.5 ANALYSIS OF PM AND PRECURSOR CONCENTRATIONS IN THE VERTICAL DIMENSION

STI-902326-2290-WP Sonoma Technology, Inc.

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#### Introduction

The questions to be addressed in Task 2.5 focus on the vertical variations of PM and PM precursors:

- 1. How do PM, precursor, and associated pollutant concentrations vary in the vertical dimension?
- 2. To what extent are ground-based measurements at higher elevations influenced by horizontal rather than by vertical phenomena?
- 3. How does vertical variation in meteorology and particle size affect the vertical distribution of PM<sub>10</sub> and PM<sub>2.5</sub>?

Air quality data from two tower sites, Angiola and Walnut Grove, and the Sierra Nevada Foothills site will be used to address the questions posed in Task 2.5. Data analysis will first focus on the tower sites because these measurements involve only vertical displacement from the San Joaquin Valley (SJV). The Angiola tower measurements will be inspected first because the tower was located in a remote area, and local sources were not expected to strongly influence the site (except when there was local farming activity). A number of gas- and particle-phase measurements were made at the Angiola tower. We expect some pollutants to display similar vertical patterns, and the variety of measurements should provide some collaborating evidence for various situations. The analysis of the Angiola data should provide a good basis for inspecting the remaining sites of interest.

The Walnut Grove tower measurements will be inspected next because these measurements also involve only vertical displacement. The Walnut Grove site was considered a transport site because emissions from the San Francisco Bay Area are transported through the area into the SJV and Sacramento Valley. With a better understanding of the vertical effects at the Angiola and Walnut Grove sites, the Sierra Nevada Foothills site will be inspected because this site involves vertical and horizontal displacement from the SJV. Analyses from IMS-95, along with results from other CRPAQS data analysis tasks, will be used to interpret vertical

variations in pollutants, draw conclusions about the observations, and possibly improve the conceptual model of pollution in the SJV.

## Scope of Work

The investigation of vertical variations in air pollution will focus on three anchor sites: Angiola ground and tower, Walnut Grove ground and tower, and Sierra Nevada Foothills. These three sites represent different site characteristics important to air quality in the SJV.

The Angiola site was located in a rural area south of Fresno. The trailer instruments were installed in January 2000, and the tower instruments were installed in August 2000; both installations were active until February 2001. The site consisted of a trailer and a 100-m tower. The trailer was extensively outfitted with gas- and particle-phase monitors. The tower had gas-and particle-phase instruments located at three elevations: approximately 1 m, 50 m, and 95 m above ground-level (agl). The air quality data, along with meteorological measurements, will be used to investigate the vertical variations in air pollution. The 24-hr filter measurements taken on a daily basis during the annual study will not be analyzed. The time resolution makes the data difficult to interpret and the data will not provide the necessary information for the questions posed in Task 2.5. We will analyze the higher resolution filter data collected during Intensive Operating Periods (IOPs).

The Walnut Grove site was located in a rural area southwest of Sacramento and was operational during the CRPAQS winter study period (from November 2000 to February 2001). The Walnut Grove site was located in a corridor allowing transport from the San Francisco Bay Area to the SJV and Sacramento Valley and vice versa. The monitoring equipment was located on the KCRA television tower at heights of 10 m and 245 m agl. In addition, limited meteorological measurements were made on the Walnut Grove tower at elevations of 9 m, 122 m, 244 m, 366 m, and 488 m.

The Sierra Nevada Foothills site was located in a rural area in the foothills northeast of Fresno and was operational during the CRPAQS winter study period (from November 2000 to February 2001). The site was located in the parking lot of a manufacturing company at an elevation of 589 m above mean sea level (msl). The site was heavily influenced by local sources: a neighbor who maintained a large bonfire on a nightly basis and painting operations at the manufacturing company. Therefore, the data must be thoroughly scrutinized to avoid drawing conclusions based on the influence of these local sources alone.

The scope of work is described in detail in the following four task elements.

## 1. Data Qualifications

We are assuming that all the data in the Central California Air Quality Studies (CCAQS) database will have undergone Level I validation. We will perform Level II validation checks in the initial phases of the data analysis. Level III sample validation is part of the data interpretation process and involves further investigation of measurements that may seem inconsistent with physical expectations. We will perform Level III validation checks whenever the need arises during our data analyses.

We will perform some accuracy and precision checks on the tower data to confirm that differences in vertical measurements are real and not the result of individual instrument variations or biases. Several periods when the mixing height is expected to exceed the height of the towers will be investigated to evaluate the accuracy and precision of the data. The mixing height is expected to be high on days with moderate wind speeds, relatively high solar radiation rates, and warm temperatures. During these periods, it is expected that ozone, NO<sub>y</sub>, PM<sub>2.5</sub> mass, PM<sub>2.5</sub> nitrate, and PM<sub>2.5</sub> black carbon will be dispersed uniformly in the vertical direction.

First, we will create time series plots of the data at the different elevations. We will use these plots to determine specific times when different relationships exist between the ground and elevated measurements. In particular, we need to determine when the air parcel sampled by instruments at different heights was well-mixed. We will then create scatter and box whisker plots to evaluate the similarity of these data. The box whisker plots will provide a measure of the comparability and consistency of the measurements among the instruments.

The comparability of the Angiola tower instruments will also be evaluated by investigating periods when the instruments were operated at the same elevation. There are two situations in which the instruments were operated in this manner. First, at the conclusion of the CRPAQS Winter Study, the Angiola tower instruments were operated side-by-side for two to three weeks to evaluate the comparability. This data will be analyzed in Task 1.1. We will use the results of the Task 1.1 analysis to qualify the measurements for assessing vertical patterns. Second, the tower instruments were brought down to ground level on a weekly basis for routine maintenance. Some of these comparisons have been made in the data validation stage. We will compare the instrument measurements made during these weekly checks to evaluate the consistency of the measurements among the instruments. For example, the nephelometer data from the 1 m, 50 m, and 90 m tower positions have been flagged as suspect as a result of poor data comparisons when the instruments were at ground level for maintenance. Therefore, the usefulness of these data is questionable. We will use the results of these analyses to qualify the data for analyzing vertical trends in the various pollutant concentrations.

# 2. Tower Data Analyses

The Angiola and Walnut Grove towers were outfitted with monitoring equipment to investigate the vertical variations in both gas- and particle-phase pollutants. After qualifying the data for applicability to tower analyses, we will analyze the data to understand the overall vertical variations and the effects of meteorology. Analyses from IMS-95, along with results from other CRPAQS data analysis tasks, will be used to complete this task. Specifically, the

mixing heights and air parcel trajectories determined in Task 5.2 will be used to evaluate the vertical variations in the pollutants.

We will evaluate the overall patterns in the data using side-by-side time series plots of the ground-level and elevated data to help answer Task 2.5 questions 1 and 3:

How do PM, precursor, and associated pollutant concentrations vary in the vertical dimension? and

How does vertical variation in meteorology and particle size affect the vertical distribution of  $PM_{10}$  and  $PM_{2.5}$ ?

We will plot meteorological data alongside the pollutant concentrations in order to evaluate the effects of meteorology. These plots will also be used to help identify PM episodes for further investigation. Results from IMS-95 and the conceptual model of air pollution in the SJV (Watson and Chow, 2001) will be used to aid in our interpretation of the time-series plots.

The observations and conclusions drawn from tower measurements during IMS-95 will be particularly useful in assessing the CRPAQS data. The IMS-95 trace gas measurements at the top and bottom of the tower revealed that when the fog extended above the instrument at the top of the tower, the concentrations of NO and  $NO_y$  were quite similar at the top and bottom of the fog layer. During a time when the top of the fog moved up and down past the trace gas instruments at 427 m, the trace gas measurements indicated that a sharp gradient in concentrations of  $NO_y$ , and ozone existed across the top boundary of the fog. The ozone concentrations were much higher and the  $NO_y$  concentrations much lower in the clear air above the fog (Richards et al., 1999).

We will use the relative humidity measurements on the tower to determine whether the measurements in this task are inside or outside the fog layer. We expect the NO and  $NO_y$  concentrations to display the same patterns as observed in IMS-95. Similar to NO in urban areas, black carbon often accumulates in the surface layer as a result of vehicular and woodburning emissions. Therefore, we expect the nighttime concentrations of black carbon to be lower in the aloft layer than on the surface. The vertical variations in  $PM_{2.5}$  and nitrate concentrations are much more difficult to predict.

Nephelometers and optical particle counters (OPCs) were operated on the ground and at elevations of 50 m and 100m. The data validation work already completed has shown that the nephelometer data from the Angiola tower are of questionable quality and may not be useful in these analyses. We will use OPC data to evaluate the vertical distribution of particulate matter as a function of particle size. The Climet OPC counts the number of particles in sixteen size bins between  $0.3~\mu m$  and  $10~\mu m$ . Basic physics suggests that the particle counts will decrease at higher vertical heights with increasing size. The vertical distribution of particles might provide insight into the source type, primary or secondary, of the PM impacting the Angiola site. We will first inspect time series plots of selected size bins from the OPC and later look at all the channels to refine the analyses. The OPC data will be extremely useful in evaluating the vertical variations in particle concentrations as a function of particle size.

The conceptual model of air pollution in the SJV will be considered when we analyze the data. Watson and Chow (2001) hypothesized that pollutants isolated in the layer above the

ground would not be removed by deposition and could be transported over distances of 50 km to 300 km on a nightly basis. According to this model, on winter nights, the concentrations of pollutants that are subject to deposition should decrease at the ground level and remain fairly steady in the aloft layer. These pollutants include ozone, PM<sub>2.5</sub> mass, and PM<sub>2.5</sub> nitrate. We will look for these patterns in the Angiola and Walnut Grove concentrations.

Watson and Chow (2001) also hypothesized that the solar intensity may be significant enough to drive photochemical reactions in the aloft layer immediately following sunrise and before sunset. These photochemical reactions might ultimately lead to the formation of particulate nitrate in the aloft layer. Abrupt increases in the particulate nitrate concentrations at the Fresno Supersite provided evidence to support this hypothesis. The tower data may also provide evidence to support this nitrate formation hypothesis. Particulate nitrate concentrations were measured on the top and bottom of both towers; we will inspect these nitrate concentrations to understand if this conceptual model is supported by the tower data. Together these analyses will provide insight for the first and third questions of Task 2.5.

# 3. Sierra Nevada Foothills Data Analyses

The Sierra Nevada Foothills site was outfitted with monitoring equipment used to investigate the variations in both gas- and particle-phase pollutants at a site that was sometimes enveloped in valley fog and, at other times, sat above the fog. We will evaluate the overall patterns in the data using side-by-side time series plots of the data to help answer Task 2.5 question 2:

To what extent are ground-based measurements at higher elevations influenced by horizontal rather than by vertical phenomena?

We will plot meteorological data alongside the pollutant concentrations in order to evaluate the effects of meteorology. The patterns observed in the Sierra Nevada Foothills time series data will be compared to the patterns observed in the Angiola and Walnut Grove data. We suspect that there will be different regimes in which vertical or horizontal phenomena dominate the concentrations observed at the Sierra Nevada Foothills site. During periods of moderate wind speeds and moderate temperatures, horizontal phenomena will likely play a more dominant role than vertical phenomena. Vertical phenomena are expected to dominate under light winds and cooler temperatures. The influence of surface deposition as pollutants move up the foothills might complicate the analyses. The Sierra Nevada Foothills time series plots will also be used to help identify PM episodes for further investigation.

## 4. Episode Analyses

We will analyze selected pollution episodes in more detail to help answer all three questions posed in Task 2.5. We will select episodes when pollution concentrations were high, and there was a multi-day buildup in pollutant concentrations. We will coordinate the selection of episodes with several CRPAQS task managers to maximize the variety of analyses performed on data from these episodes and, thus, strengthen the understanding of air pollution episodes in the SJV. For these episodes, we will inspect backward trajectories and mixing heights estimated

in Task 5.2. We will use the backward trajectories to help determine the origin of air parcels impacting the tower sites.

#### Time Line

If all the air quality and meteorological data are available from the CCAQS database, Task 2.5 will commence in February. Some of the data qualifications in task element 1 can be performed without input from other tasks, although the results from Task 1.1 will be very important in task element 1 and will be critical for the completion of the subsequent task elements. The tower data analyses and Sierra Nevada Foothills data analyses (task elements 2 and 3) will begin in March, assuming the backward trajectories and mixing heights needed from Task 5.2 will be available in time. The CRPAQS data analysis project managers will collectively select the episodes for analysis based on ARB reports and preliminary analyses. The episode analyses (task element 4) will be performed next. Task 2.5 findings will be documented and a draft final memorandum will be delivered in July 2003. Depending on the time line for reviewers' comments, the final memorandum will be delivered at the end of August 2003. The manuscript for the peer-reviewed publication will be submitted in September 2003, and the findings will be presented at a technical conference in fall 2003.

#### **Schedule of Deliverables**

**Table 1** lists the deliverables to be prepared under Task 2.5 and their planned due dates.

Deliverable	Deliverable Due Date
Draft work plan	December 2002
Final work plan	January 31, 2003
Draft final memorandum summarizing findings	July 31, 2003
Final memorandum summarizing findings	August 31, 2003
Manuscript for publication	September 30, 2003
Meeting presentation	Fall 2003

Table 1. Estimated schedule of deliverables.

#### **Description of Deliverables**

- A draft final memorandum consisting of a manuscript to be submitted to a peer-reviewed publication and one or more appendices that include data and discussions not included for the publication.
- A final memorandum incorporating reviewers' comments.
- A paper to be submitted for publication based on the memorandum.
- A presentation for a technical conference (e.g., 2003 AWMA Annual Conference).

# **ARB Staff Assigned to this Task**

The ARB Project Manager assigned to this task is

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# **STI Staff Assigned to This Task**

The STI Project Manager is Lyle R. Chinkin. The STI Task Manager assigned to this task is Nicole P. Hyslop.

### Data Products to be Performed/Delivered by ARB

ARB will not be required to perform any work for Task 4.3.

#### Software and Models to be used by STI

We will use the COARSE on-line system, Microsoft Excel spreadsheets, Microsoft Access databases, and Systat statistical analysis software to perform the described analyses. All of these products are currently installed at STI.

#### Models, Reports, or Other Data to be supplied to STI by ARB

To conduct the Task 2.5 analyses, we will require the following elements:

- Continuous and non-continuous air quality measurements for the Angiola, Walnut Grove, and Sierra Nevada Foothills sites, listed in Tables 1 and 2.
- Meteorological measurements made on the ground and towers at the Angiola, Walnut Grove, and Sierra Nevada Foothills sites.

Table 1. Continuous measurements made at the Angiola, Walnut Grove, and Sierra Nevada Foothills sites.

	Site	Angiola	Angiola	Angiola	Angiola	Walnut Grove	Walnut Grove	Sierra Nevada
ID	Instrument	Trailer	1 m	50 m	95 m	10 m	245 m	Foothills
A	Nephelometer	2/1/00-2/16/01	2/14/00-3/15/01	8/18/00-2/12/01	8/4/00-2/16/00	1/1/00-2/20/01	11/26/00-2/13/01	11/2/00-2/8/01
G	Aethalometer	1/12/00-3/29/01	-	_	11/21/00-2/16/01	11/13/00-2/13/01	11/16/00-2/13/01	11/19/00-2/14/01
Ι	Climet Optical	3/30/00-2/8/01	_	8/18/00-2/12/01	8/18/00-2/16/01	_	_	
	Particle Counter							
J	PM <sub>10</sub> BAM	1/21/00-3/29/01	-	_	-	-	-	11/19/01-2/12/01
K	PM <sub>2.5</sub> BAM	1/21/00-3/29/01	_	_	_	_	_	11/19/01-2/12/01
N	PAN/NO <sub>2</sub>	11/19/00-2/12/01	_	_	_	_	_	11/10/00-2/13/01
О	NO <sub>y</sub>	12/20/99-2/23/01	_	_	12/1/00-2/23/01	_	_	11/16/00-2/15/01
P	O3	1/22/00-2/21/01	_	_	11/30/00-2/21/01	_	_	11/3/00-2/13/01
Q	Nitrate	11/19/00-3/2/01	_	_	12/4/00-3/2/01	11/10/00-2/13/01	11/16/00-2/13/01	11/20/01-2/12/01
R	HNO <sub>3</sub>	11/21/00-2/26/01	_	_	_	_	_	11/16/00-2/15/01

Table 2. Non-continuous measurements made at the Angiola and Sierra Nevada Foothills sites.

ID	Instrument	Angiola Trailer	Sierra Nevada Foothills
b, c, d	MOUDI	11/19/00-2/6/01	_
L	SFS	12/31/99-2/6/01	11/30/00-2/6/01
S	SGS	11/30/00-2/6/01	11/30/00-2/6/01
U	Light hydrocarbons	11/19/00-2/6/01	12/1/00-2/6/01
V	Heavy Hydrocarbons	11/19/00-2/6/01	11/19/00-2/6/01
W	PM <sub>2.5</sub> Organics	11/19/00-2/6/01	11/19/00-2/6/01
X	Carbonyls	12/15/00-2/3/01	11/21/00-2/6/01

# References

- Richards L.W., Dye T.S., Ray S.E., and MacDonald C.P. (1999) Effects of atmospheric dynamics and chemical concentrations on aerosol formation in fog. Report prepared for the San Joaquin Valleywide Air Pollution Study Agency, California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Petaluma, CA, STI-95093-1859-FR2, April.
- Watson J.G. and Chow J.C. (2001) A wintertime PM<sub>2.5</sub> episode at the Fresno, CA, Supersite. *Atmos. Environ.* **36(3)**, 465-475.